Modified Test 7 Conditions for EVA Applications

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Background

- Traditional Offgas Test
  - Conducted at elevated temperatures (120°F) over a specified period of time (72 hours) to evaluate potential off-gas products that may contribute to contamination in a closed environment
  - Results compared to 7-day spacecraft maximum allowable concentrations (SMACs) and required to meet a T-value criteria (the sum of the ratio of measured concentrations to their SMAC) of < 0.5

The Issue

- When offgassing evaluations using the free volume inside the EMU were implemented, it was recognized that the standard test conditions are overly conservative for EMU applications.
  - EVAs are limited to a much shorter duration of exposure
  - Maximum temperature inside the vent loop is certified at 90°F
    - Temperatures are not expected to exceed 75°F nominally.
  - Application of 7-day SMACs is conservative for an 8-hour EVA
    - Shorter-term SMACs exist (1-hour and 24-hour), but they are intended to apply to off-nominal situations and are therefore not appropriate for EMU.

- Therefore, the JSC Toxicology and Environmental Chemistry group was asked to evaluate off-gas test procedures for the EMU and issue recommendations for future testing.

Recommendation

Test	Temperature	Duration	Volume	SMAC
Standard	120°F	72 hours	0.14 m^3	7-day values x 10
Alternate	100°F	24 hours	0.14 m^3	7-day values

- Alternate test temperature exceeds the certification temperature (90°F) but was deemed reasonably conservative because it generally corresponds with human body temperature.
- Alternate test duration was determined based on the length of a working day. A 10-12 hour test would likely be sufficient but would require overtime or schedule shifting every time a test was performed.
- Conditions remain conservative for both the standard and alternate test conditions, so the free volume of the EMU (5 ft^3 or 0.14 m^3) is applied.
- In the case of the standard off-gas test conditions, an additional modifying factor of 10 may be applied to account for the extremely conservative nature of the test.

Offgas Temperature Update

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Background

- NHB-8060 listed the offgas conditioning temperature as 120 ± 5°F (49 ± 3°C)

- NASA-STD-6001 listed the offgas conditioning temperature as 50 ± 3°C (120 ± 5°F)

> b. Specimens shall be placed into certified-clean sealed containers and thermally conditioned for 72 (±1) hr at 50 (±3) °C (122 (±5) °F).

Survey

- WSTF discussed with JSC M&P to determine.
  - Is the intent to change the offgas conditioning temperature from the historic temperature?
  - Would it be possible to change back to the historic temperature?
- WSTF was tasked with surveying other NASA labs to determine what set-point was used for temperature conditioning.

Results

- All 3 NASA labs have continued to use 120°F as the temperature conditioning set-point.
- It was decided by JSC that continued use of the historic set-point is acceptable.
- NASA-STD-6001 will continue to list 50 °C as the set-point, however the range will be updated to ± 4°C during the next revision.

Rationale

- Expanding the offgassing tolerance to 50 +/-4 ^{0}C would allow NASA centers to maintain the historical parameters while allowing international laboratories controlling to 50C to also fall within requirements.
- This expansion in tolerance is not seen as a technical impact as the large data method variations seen during round robin testing (largely attributed to analytical method known variability) well encompasses any variations that may result from an expanded temperature tolerance during sample conditioning.

Question

- What set-point does JAXA use for Test 7 conditioning temperature?

Extending the Life of Gas Standards

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Introduction

- Historically most gas standards at WSTF were given expiration dates by the manufacturer of 6 months – 1 year.
- Historical requirements required WSTF to maintain all gas standards within manufacturer's expiration dates
  - This proved very costly as well as time-consuming to continuously order the multiple standards maintained at WSTF.

Recertifying Gas Standards

- In 2009, WSTF began sending some expired gas standards back to the manufacturer for recertification.
  - Pros:
    - There was a 25% cost savings compared to ordering a new standard.
    - Data was generated to show gas standards are “good” well past their manufacturer expiration date and the manufacturer agreed to extend these dates to longer durations.
  - Cons:
    - More storage space was needed to maintain duplicate gas standards to allow one to be sent back for recertification.
    - Duplicate standards generated more cylinder rental fees.
    - 500 psi was required, so not all could be recertified.

Mix A

- 2 different Mix A cylinders (ALM061923 & ALM000197) were recertified by the manufacturer. Data for ALM061923 below.
- The manufacturer did not change the concentrations of the components in either cylinder during recertification.

ALM061923 Component	3/27/07 Manufacturer Original Concentration (ppb)	3/11/09 Manufacturer (Re)Certified Concentration (ppb)	7/15/11 Manufacturer (Re)Certified Concentration (ppb)
Carbon Tetrachloride	4.99	4.99	4.99
1,1-Dichloroethylene	4.96	4.96	4.96
Ethanol	9.99	9.99	9.99
Isopropyl Alcohol	10.0	10.0	10.0
Methanol	10.1	10.1	10.1
Tetrachloroethylene	10.0	10.0	10.0
Toluene	10.1	10.1	10.1
Trichloroethylene	5.00	5.00	5.00
Vinyl Chloride	5.07	5.07	5.07

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** All expiration dates were 1 year from analysis date.

*** Accuracy ± 5%

Mix B

- 1 Mix B cylinder was recertified by the manufacturer.
- The manufacturer did not change the concentrations of the components.

ALM047004 Component	2/19/08 Manufacturer Original Concentration (ppb)	4/14/10 Manufacturer (Re)Certified Concentration (ppb)
Acetaldehyde	5.29	5.29
Acetonitrile	5.44	5.44
Acrolein	5.34	5.34
Acrylonitrile	5.38	5.38
Benzene	5.26	5.26
1-Butene	5.25	5.25
1,4-Dioxane	5.18	5.18
Methyl Ethyl Ketone	5.36	5.36
Methyl Isobutyl Ketone	5.42	5.42
Propanal	5.17	5.17

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** All expiration dates were 1 year from analysis date.

*** Accuracy ± 5%

Mix B'

- 1 Mix B' cylinder was recertified by the manufacturer.
- The manufacturer did not change the concentrations of the components.

ALM018238 Component	3/28/07 Manufacturer Original Concentration (ppb)	4/14/10 Manufacturer (Re)Certified Concentration (ppb)
Acetone	10.9	10.9
Furan	10.0	10.0
Furfural	10.9	10.9

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** Original Expiration date was 2 years from analysis date. Recertifed expiration date was 1 year from analysis date.

*** Accuracy ± 5%

Formaldehyde PPB

- The expiration date from the manufacturer for this gas standard was inconsistent, varying from 6 months – 2 years.
- Concentration changes were acceptable.

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppb)	RPD
3/3/2008	9/1/2008	780	N/A
8/24/2009	2/22/2010	740	5.13
8/12/2012	2/10/2012	770	1.28

* Accuracy ± 10%

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppb)	RPD
9/23/2008	9/23/2009	620	N/A
4/20/2010	4/20/2011	600	3.23

* Accuracy ± 10%

Formaldehyde PPM

- The expiration date from the manufacturer for this gas standard varied from 6 months – 1 year.
- Concentration changes were acceptable.

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppm)	RPD
3/3/2008	9/1/2008	11.2	N/A
4/19/2010	4/19/2011	10.7	4.46

* Accuracy ± 10%

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppm)	RPD
2/16/2009	2/16/2010	9.6	N/A
8/11/2011	8/10/2012	8.7	9.38

* Accuracy ± 10%

Ammonia

- 2 different cylinders of Ammonia were recertified by the manufacturer.
- Concentration changes were acceptable.

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppm)
3/28/2007	3/27/2008	21.1
3/27/2009	3/27/2010	21.1

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** Accuracy ± 5%

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppm)	RPD
3/8/2008	3/24/2009	21.1	N/A
5/7/2010	5/7/2011	20.32	3.70

* Accuracy ± 5%

PPB Mix

- PPB Mix expiration date is only 6 months.
- There was no change in concentrations when recertified by the manufacturer 2 years later.

Component	11/17/08 Manufacturer Original Concentration (ppb)	1/13/10 Manufacturer (Re)Certified Concentration (ppb)
Acrolein	525	525
Benzaldehyde	532	532
Benzene	527	527
Furan	527	527
MBK	529	529
MVK	521	521

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** All expiration dates were 6 months from analysis date.

*** Accuracy ± 5%

Hydrogen Cyanide

- There was no change in concentration when recertified by the manufacturer 2 years later.

Certification Date	Manufacturer Expiration Date	Manufacturer (Re)Certified Concentration (ppm)
7/18/2007	7/17/2008	5.2
7/8/2009	1/8/2010	5.2

* Manufacturer stated if reanalyzed concentration was "within a certain range", the original concentration was reported.

** Accuracy ± 5%

Recertification Summary

- The concentrations of all components in the recertified gas standards remained stable during the 5 years data was accumulated.
- WSTF developed a procedure for tracking the gas standards to allow use past the manufacturer expiration dates.
- In 2013, the manufacturer independently extended expiration durations to 3 years for most gas standards ordered by WSTF.

Letter from Manufacturer

- Confirmation that the manufacturer expiration date is a “warranty” not a shelf-life date.

August 28, 2012

Vanessa,

This letter is in response to your question regarding the expiration date listed on cylinders. The expiration date listed is not necessarily a shelf life on the gas but a warranty period. The gas will not go bad on the date listed. If something were to happen to the gas (due to the manufacturing of the mixture or a defect on the cylinder/valve) during the period from the date it was certified to the expiration date, we would take care of the problem for you. If you have some reactive gases such as Nitric Oxide, Ammonia, or Sulfur Dioxide, it would be a good idea to monitor their performance or to periodically get these re-certified because these components have a greater chance of changing over time. Components such as Oxygen and Carbon Dioxide are very stable and as long as the cylinder is properly maintained, will not change concentrations over time. The same can be said for Natural Gas Mixtures. As long as the dew point is not reached, the gas will be fine. If you have further questions, please feel free to contact me.

303-651-3910 ext. 117 or at devon.vonfeldt@airliquide.com

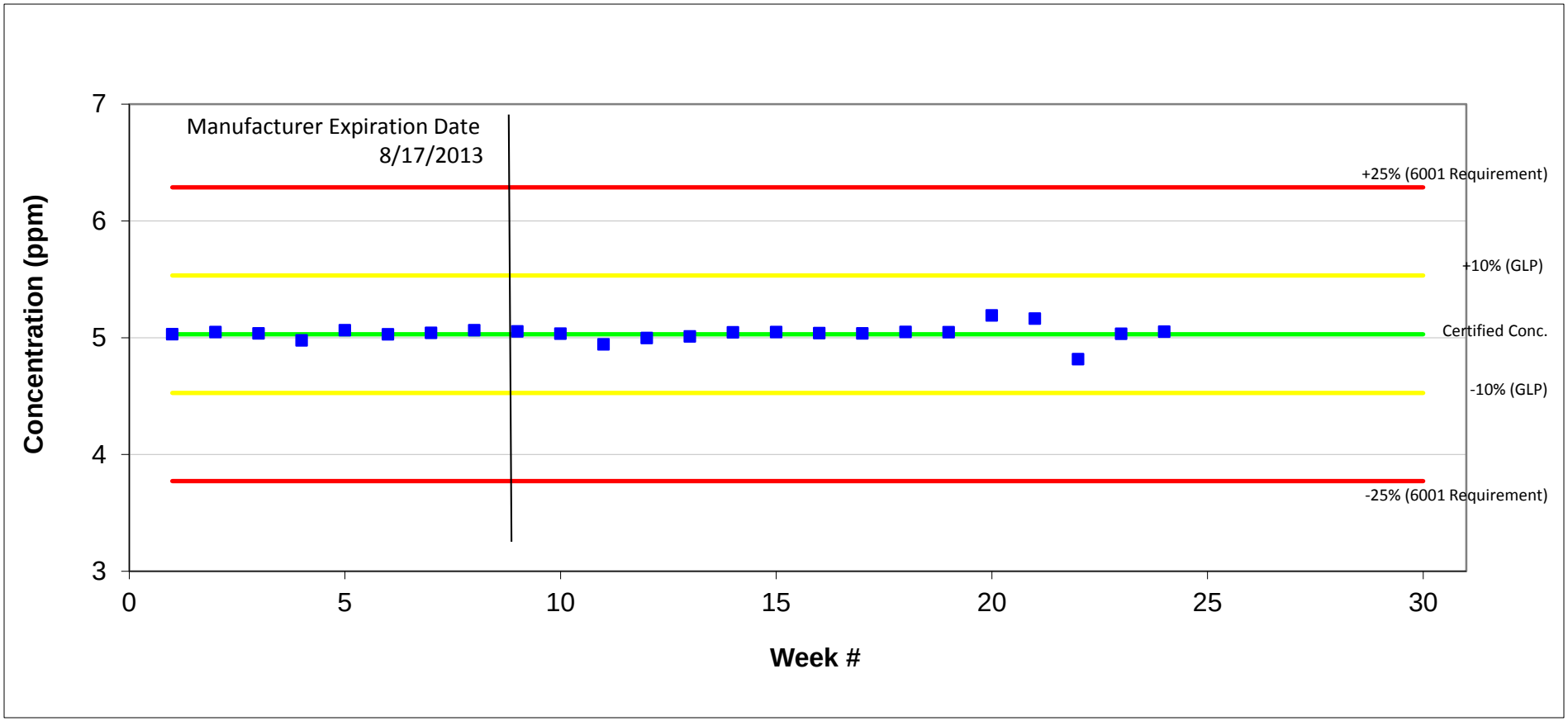
Sincerely,

Devon VonFeldt
Quality Assurance Manager

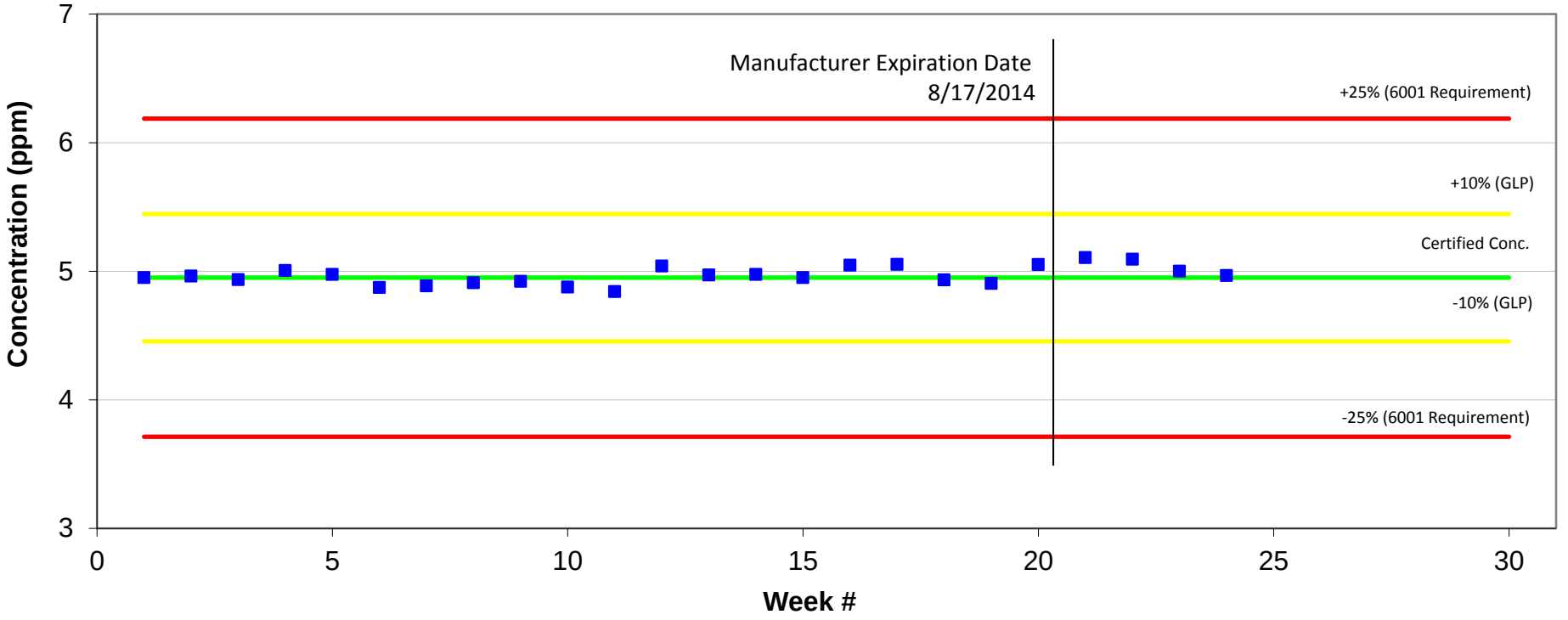
Usage Life Extension

- A primary instrument calibration standard is maintained within manufacturer expiration period.
  - GC/FID/TCD – CO, CH_4, H_2
  - GC/FID – Propane
  - GC/MS – d-6 Benzene, Bromofluorobenzene
- The primary instrument calibration standard response is tracked to ensure proper instrument performance.
- Components of gas standards used for Test 7 quantification are tracked in individual performance charts.
  - Performance is continuously monitored allowing use after manufacturer expiration date.

Chloroethylene Performance Chart



Butene Performance Chart



Questions

- Does JAXA use gas standards ordered from a manufacturer?
  - Are they used past manufacturer expiration dates?

2014 GLP Data

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Gas Standards GLP Data

		Precision	Accuracy
	Requirement:	(ISO-No Specification) (WJI-10% or SIC Approval)	(ISO/WJI ± 25% with 6001 exceptions* ± 30%)
NASA GLP Compounds (ISO Table 1)	**Standard Conc. (ppm)**	**% RSD** (at standard conc.)	**Avg. % Recovery** (at standard conc.)
1,4-dioxane	5.26	1.09	99
1-butene	4.95	0.27	100
acetaldehyde	5.10	1.56	84
acetone	10.1	2.00	100
acetonitrile	5.18	3.58	86
acrolein	5.22	6.87	98
acrylonitrile*	4.67	1.04	97
benzene	5.17	0.30	101
dichloroethylene	5.23	1.30	104
ethyl alcohol*	10.4	1.15	95
furan	9.97	0.52	103
furfural (not required)	10.1	20.55	101
isopropyl alcohol	10.3	0.86	97
methyl alcohol*	10.4	9.88	90
methyl ethyl ketone	5.14	0.53	98
methyl isobutyl ketone	5.04	0.92	101
propionaldehyde (propanal)	5.08	0.27	102
tetrachloroethylene*	10.1	7.57	95
tetrachloromethane*	4.96	3.97	85
toluene	10.1	5.80	96
trichloroethylene	5.15	4.00	98
vinyl chloride (chloroethylene)	5.03	0.27	100

- All compounds are within required specifications. Furfural not required.

Material GLP Data

46263 Nomex (2013)	µg/g	46474 Nomex (2014)	µg/g	Average	RPD
Chloromethane	0.0459	Chloromethane	0.0282	0.0371	47.7
Acetaldehyde	0.0989	Acetaldehyde	0.0376	0.0683	89.8
Butene	0.0018	Butene	ND	0.0018	N/A
n-Butane	0.0093	n-Butane	0.0066	0.0079	34.1
Acetone	0.3358	Acetone	0.0908	0.2133	114.8
3-Chloro-1-propene	0.0183	3-Chloro-1-propene	ND	0.0183	N/A
Dichloromethane	0.1090	Dichloromethane	0.0125	0.0607	159.0
Isobutyraldehyde	0.0062	Isobutyraldehyde	0.0054	0.0058	14.6
Unidentified component	0.0096	Unidentified Component	ND	0.0096	N/A
1,1-Dichloroethylene	ND	1,1-Dichloroethylene	0.0108	0.0108	N/A
Butyraldehyde	0.0047	Butyraldehyde	0.0103	0.0075	75.5
Methyl ethyl ketone	0.0169	Methyl ethyl ketone	0.0055	0.0112	102.1
Ethyl acetate	0.0901	Ethyl acetate	0.0053	0.0477	177.8
3-Methylbutanal	0.0084	3-Methylbutanal	0.0065	0.0074	25.9
Pentanal	0.0258	Pentanal	0.0132	0.0195	64.5
1,2-Dichloropropane	0.0060	1,2-Dichloropropane	ND	0.0060	N/A
Toluene	0.0075	Toluene	0.0016	0.0045	129.8
n-Hexanal	0.0251	n-Hexanal	0.0179	0.0215	33.7
Hexamethylcyclotrisiloxane	ND	Hexamethylcyclotrisiloxane	0.0204	0.0204	N/A
Heptanal	ND	Heptanal	0.0210	0.0210	N/A
Octamethylcyclotetrasiloxane	ND	Octamethylcyclotetrasiloxane	0.0284	0.0284	N/A
Nonanal	ND	Nonanal	0.0256	0.0256	N/A
Carbonyl Sulfide	ND	Carbonyl Sulfide	0.0072	0.0072	N/A
				Average RPD	**82.3**

- Material is over 1 year old and all original offgassed quantities are small, so high RPD are expected.
- New MS allows identification of later eluting compounds